DOCUMENT-IDENTIFIER: US 5660624 A
TITLE: Self-repairing, reinforced matrix materials

Abstract Text (1):
Self-repairing, fiber reinforced matrix materials include a matrix material including inorganic as well as organic matrices. Disposed within the matrix are hollow fibers having a selectively releasable modifying agent contained therein. The hollow fibers may be inorganic or organic and of any desired length, wall thickness or cross-sectional configuration. The modifying agent is selected from materials capable of beneficially modifying the matrix fiber composite after curing. The modifying agents are selectively released into the surrounding matrix in use in response to a predetermined stimulus be it internal or externally applied. The hollow fibers may be closed off or even coated to provide a way to keep the modifying agent in the fibers until the appropriate time for selective release occurs. Self-repair, smart fiber matrix composite materials capable of repairing microcracks, releasing corrosion inhibitors or permeability modifiers are described as preferred embodiments in concrete and polymer based shaped articles.

Brief Summary Text (5):
Various techniques have been suggested in the past for overcoming these drawbacks. The addition of fibers to concrete has improved its tensile strength but has decreased its compression strength. Providing exterior coatings on the outer surfaces of the concrete has reduced water permeation, but it is a time-consuming additional step and has little, if any, effect on the lasting strength of the concrete. The addition of modifying agents as freely-mixed additives into a concrete mixture before setting has also been tried. These efforts have met with generally unsatisfactory results. Attempts to add modifying agents in the form of micronodules or prills have also been tried. Frequently, the prills are designed to be heat melted to cause release of the modifying agent into the matrix after setting of the materials. These designs require the application of heat to release the beneficial additive into the matrix after cure. Moreover, the melted, permeated agents leave behind voids in the concrete which weakens the overall structure under load. Accordingly, a demand still exists for an improved concrete matrix material having greater tensile strength, greater durability and comparable or improved compression strength.

Brief Summary Text (7):
As used herein, matrix composite materials may refer to generally any continuous matrix phase whether it comprises a settable construction material such as cementitious materials or a thermoplastic material such as asphalt materials, as well as, other synthetic or natural high polymer materials, ceramics, metals and other alloy materials. The matrix composite materials include various fiber reinforcements therein distributed throughout the matrix or placed at desired locations within the continuous phase. The matrix composite materials may be fabricated as large building structures and load bearing shaped articles, or they may be molded or machined as small parts for specialty uses. For example, the matrix material may comprise a thin sheet or web of material in the form of a foil, wrap, tape, patch or in strip form. As presently used in this specification, the term matrix composite material does not necessarily refer to large civil engineering structures such as highways and bridges.

Brief Summary Text (8):
In connection with the polymer and/or metal or ceramic matrix composite materials, as well as, in the settable building materials such as concrete materials, special problems cause structures made from these materials to become aged or damaged in use. More particularly, special structural defects arise in use including microcracking, fiber debonding, matrix delamination, fiber breakage, and fiber corrosion, to name but a few. Any one of these microscopic and macroscopic phenomena

may lead to failures which alter the strength, stiffness, dimensional stability and life span of the materials. Microcracks, for example, may lead to major structural damage and environmental degradation. The microcracks may grow into larger cracks with time and cause overall material fatigue so that the material deteriorates in long-term use.

Brief Summary Text (23):
The principles of the present invention are applicable to space age polymer, metal and/or ceramic structural matrix composite materials as well as more conventional cementitious settable or curable building or construction materials.

Drawing Description Text (3):
FIGS. 2a-2e are schematic views of the new and improved self-repairing fiber reinforced matrix composite material in accordance with this invention, illustrating a smart matrix repair sequence of salt or pH change penetration into the matrix adjacent a smart fiber wrapped rebar reinforcement causing dissolution of the pH sensitive coating, thereby releasing anticorrosion modifying agents in the domain or vicinity of the rebar to prevent corrosion of the rebar and showing the smart fiber wrapped rebar disposed in a matrix prior to chemical intrusion in FIG. 2a, intrusion of chloride or carbon dioxide into the matrix and causing a pH change in the matrix in FIG. 2b, a breakdown of pH sensitive coating on the smart fibers caused by pH changes in the matrix due to chemical intrusion in FIG. 2c, subsequent release of the anti-corrosion chemical from the smart fibers now rendered porous due to the breakdown of the coating in the viscinity of the rebar in FIG. 2d and illustrating released chemical corrosion protection chemicals around the rebar and preventing corrosion of the rebar in FIG. 2e;

Drawing Description Text (5):
FIG. 4 is a schematic view of the new and improved smart fiber reinforced matrix composite material in accordance with the present invention, illustrating a release, repair mechanism in which the fiber is debonded from the coating and matrix in response to an applied load to release the modifying agent from the uncoated fiber pores;

Drawing Description Text (31):
FIG. 23e is an alternate embodiment of the type shown in FIG. 23d wherein the electrode adjacent to the rebar is capable of causing smart fiber release of charged zinc ions to coat the rebar in an electroplating operation to prevent corrosion of the rebar once the ingress of water or moisture is detected;

Drawing Description Text (35):
FIGS. 27a and 27b show another alternate embodiment of this invention wherein the smart repair fiber comprises an assembly of an outer glass tube and an inner metal fiber member in an optical fiber and an adhesive modifying chemical therein as shown in FIG. 27a, which in response to an applied cracking load ruptures the glass fiber to repair the crack while maintaining the optical fiber in an altered, but undamaged condition as shown in FIG. 27b;

Detailed Description Text (2):
In accordance with the present invention, new and improved shaped articles comprise curable, settable, cross-linkable and/or hardenable matrix materials. The matrix material comprises a continuous phase and is a material that may be shaped to form a three-dimensional shaped article adapted for a particular use. Matrix materials can include any curable, settable or hardenable materials used in construction, building, roofing, roadway, aircraft, automotive, marine, appliances, transportation and/or biomedical fields for making shaped articles. Typically these materials will be moldable or castable to form shaped objects or may be laminated or assembled into finished products. The matrix materials may be inorganic or organic in nature and may include by way of illustration: cement, concrete, sintered fly ash or bottom ash/phosphoric acid mixtures, ceramics including, for example, silicon oxide, titanium oxide, silicon nitrite, graphite, carbon, and metals such as aluminum, steel or other metal alloys, asphalt, thermoplastic polymers, thermosetting polymers, thermoplastic elastomers, crosslinkable polymers, curable polymer resin systems and hydroxyapatite. Illustrative thermoplastic polymers include polyolefins, polyesters, polycarbonates, polyacrylates, polyarylates, polyamides, polyimides, polyaramides, polyurethanes, foaming polyurethane compositions and any other thermoplastic polymers used as engineering thermoplastics for making shaped articles. Thermosetting and crosslinkable polymers and curable resin systems may include, for example, one and two part epoxies, phenolformaldehyde resins and other

thermosetting and crosslinkable polymers. Thermoplastic elastomers can include rubbery polymers and copolymers including, for example without limitation, styrene-butadiene, rubber, neoprene, SEBS, NBR, and, EPDM rubbers and the like. Visco-elastic materials and various latex materials may also be used. The matrix materials may also comprise sinterable ceramic materials including hydroxyapatites, as well as, other ceramic materials such as silicas, titanium, carbides, oxides and alumina. The matrix materials may also comprise metal matrices including aluminum, iron, lead, copper, steel, bronze, phosphor bronze, brass and other alloys, as well as biomimetic systems like bone matrices formed of various calcium salts, as well as other organic and inorganic materials.

Detailed Description Text (4):
The new and improved shaped articles of this invention additionally comprise hollow fibers having interior spaces therein for containing selectively releasable modifying agents. The hollow fiber materials may include inorganic fibers or organic fibers. Illustrative inorganic fibers include, without limitation: fiberglass fibers, cement fibers, asphalt fibers, hydroxyapatite fibers, glass fibers, ceramic fibers, metal fibers, and the like. Illustrative organic fibers that may be used as the hollow fiber component may include, without limitation: polyolefin fibers, polyester fibers, polyamide fibers, polyaramide fibers, polyimide fibers, carbon fibers, graphite fibers, cellulose fibers, nitrocellulose fibers, hydrocarbon fibers, GORETEX.RTM. fibers, KEVLAR.RTM. fibers, and the like, to name but a few. Porous polypropyline fibers are a preferred hollow fiber. The hollow fibers may be elastomeric.

Detailed Description Text (5):
The fibers may be bundled, woven or loose. They may be held or engaged together with flexible web materials. They may comprise twisted pairs and additionally may include concentric structures of one or more fibers. The sidewalls of the fibers are typically rupturable or porous to permit the discharge or exiting of the modifying agent into the surrounding cured composite matrix material. The fibers may come in different shapes, volumes, and wall thicknesses. They may be generally notched, have periodic enlargements or bulges, V-shaped, double or multiple lumens, U-shaped, or they may comprise combinations of one or more different types of fibers. For example, double walled fibers are particularly useful for two-part modifying compositions such as epoxies. Doubled fibers including a metallic inside fiber and a glass outer sheath fiber are useful where bending of the metal fiber assists in breaking the glass carrier fiber. Additionally, assembled structures of polypropylene hollow porous fibers disposed inside a glass outer fiber might be used to permit a first break and release of modifying material to occur with the glass fiber and thereafter a secondary break and release of the polypropylene fiber at a later date to provide specially long-term profile modification to the shaped matrix composites. The smart-release fibers may also be paired or include other specialty fibers such as piezoelectric fibers or optical sensor fibers for providing special monitoring, metering and diagnostic capabilities. Some of these specialty composites will be more particularly described hereinafter. The fibers may also be woven together into a web so that they may be wrapped as an organized bundle around rebars or the like. Although fiber materials are preferred, other container-like smart release structures or vessels may be provided for special end uses. For example, in relatively large structural parts it may be useful to add the repair chemicals in large flat balloons or bags layered or laid up within the matrix or layers of matrix. It should be apparent to those skilled in this art that for certain end uses, small release vessels having a shape somewhat different from hollow fibers for performing the same smart release functions may be employed. In addition, the fibers may be relatively small, chopped or comminuted fibers having lengths of less than about one inch and diameters of less than about 100 microns. The fibers and matrices may be readily used in usual shaping processes such as in an injection molding operations or the like.

Detailed Description Text (16):
In accordance with this invention, means are provided for maintaining the modifying agent within the hollow fibers. The modifying agents may be physically trapped by, for example, drawing liquid additives into the interior of the fibers and retaining them therein by capillary action or by closing off the ends of the fibers. For brittle fibers, sealing of the ends by heat or pressure may be one method for maintaining the modifying agents therein. Moreover, specialty coatings may be used, which will selectively degrade upon the occurrence of a particular external stimulus. Illustrative examples might include heat sensitive coatings, pH sensitive coatings, ion sensitive coatings, and the like. These coatings are effective to

close off the pores of the hollow fiber walls or the ends of the fibers to prevent premature leakage of the modifying agent until the intended time. Illustrative coatings may include waxes, low molecular weight hydrocarbon oils and coating polymers to name but a few. More particularly, the coatings may include chemically sensitive coatings, electrically sensitive coatings and/or radiation sensitive coatings. Chemically sensitive coatings may include moisture sensitive coatings, pH sensitive coatings, ion sensitive coatings or solvent sensitive coatings. Electrically sensitive coatings may include current sensitive coatings or voltage sensitive coatings. Radiation sensitive coatings may include light sensitive coatings, temperature sensitive coatings or radioactivity sensitive coatings.

Detailed Description Text (17):
In accordance with the present invention, means for permitting selective release of the modifying agent in response to the external stimulus may be provided. Illustrative examples include the selectively removable or dissolvable coatings which give way to permit leakage of the modifying agent in response to, for example, stimuli such as heating, cooling, loading, impacting, cracking, water infusion, chloride infusion, alkalinity changes, acidity changes, acoustic excitation, low frequency wave excitations, hydrostatic pressure, rolling pressure, light sensitivity or laser excitation, or the like. Electrical currents, voltages, electrorheological excitation, radiation, or other energetic stimuli may also be employed or effective to permit or cause selective release of the modifying agent or agents from the fibers.

Detailed Description Text (22):
The shaped articles of this invention might also be useful in biomedical applications as bone replacements as prosthetic devices and as biomedical adhesives.

Detailed Description Text (24):
In accordance with this biological models, the present invention may be employed to provided a self-growing structure something like bone, wherein the hollow pores polymer fibers may release chemicals and act as an organic template on which to form a strong structural bone-like composite. This self-growing structure might be used for structural materials as well as for computer chips or for prosthetic devices. More particularly, just as ligaments or tendons have been used as natural matrices to form bone materials, these polymer tubes or fibers are used in accordance with the present invention to concentrate bone-like substances. The fibers are hollow and have porous walls. In accordance with this invention chemicals are released from the hollow fibers, particularly polymeric materials which are designed to cause targeted release of water in an inorganic matrix to form a structural network of calcium phosphate materials. Instead of using collagen gels to form a backbone network, in accordance with this invention, a matrix material including inorganic cementitious salts and a first polymer reactant may be provided which includes hollow fiber materials including a condensable or cross-linkable moiety reactive with polymer. Under appropriate conditions, release of the co-reactant from the fibers causes a condensation reaction of the matrix polymer in which water is produced. The water byproduct of the condensation reaction is used to hydrate cement to build up a structural backbone along the fiber regions.

Detailed Description Text (27):
In accordance with this invention, materials may be developed for application in self-repairing materials for use in facings, coatings and membranes. In accordance with this aspect of the invention, the new and improved fiber-containing matrix materials may be provided in the form of paints, membranes, roofing materials, or the like, including self-repairing liquids within the fibers. The materials may be provided in the form of wraps for buildings, bridges, roads, or the like, including webs or fabrics of smart fibers disposed within the matrix. Repair chemicals may repair cracks in the wrap itself or also seep into and repair adjacent structures to which the wrap is adhered to improve the overall structural performance over time. Specialty wraps including solar collecting fibers might also be added to the exterior of previously existing outdoor structures.

Detailed Description Text (30):
The shaped articles of this invention may also be used in various small shaped article applications including aerospace applications, pipe repair, engine pistons, rubber matrices, waterborne paints and coatings, rubber gasket materials and other seals and in woven fabrics. For example, in fabrics the fibers may contain a fabric glue to repair small tears or abrasions of the fabric. Hard self-repairing shaped

articles, such as silicon nitride fibers in carbon-alumina matrices for pistons might be used. Metal matrices that may be employed include metals and alloys such as alumina as well as foamed metals. The fibers for these metallic composites may include adhesive materials or corrosion resistant materials to help repair the matrices or other desirable smart release additives.

Detailed Description Text (32):
In a related application, the new and improved smart matrix materials may be used to perform road repair and pothole repair. In connection with this aspect, smart release fiber-containing uncured material may be added to a pothole. An agitation or pressure may be used to release curative agents from the interior of fibers provided in the matrix material to promote adhesion and curing of the pothole repair mass to the substrate road surface. Additional fibers may be provided containing repair adhesives which release in response to tire pressure, to further strengthen and reinforce the pothole patch in use.

Detailed Description Text (37):
Another special useful application of the shaped articles in accordance with this invention is as a containment structures for radioactive or chemical waste materials. In accordance with this aspect, fibers provided with chemically sensitive coatings or radiation sensitive coatings may be provided which are adapted to release scavenger compounds when radiation or chemical waste is detected. The compounds will then migrate from the fibers into the matrix to scavenge and render harmless radioactive or chemical materials leaking into the containment vessels to prevent them from being discharged from the containment area into the environment. Alternatively, permeability modifying agents may be released from the coated fibers to boost the impermeability of the containment vessel to water-borne contaminants.

Detailed Description Text (39):
As has been mentioned above, various means may be provided to force the repair chemicals out of the fibers. Chemicals may be pumped into hollow fibers from the outside or propellant gases may be injected into previously filled fibers to which external access has been provided to force the chemicals out. Other methods to promote repair chemical release may include electrical, magnetic, and chemical means which alter the shape, permeability or coating integrity of the fibers. Shaped memory alloy materials may be used as the fiber or these materials may be used in the fiber to squeeze the fiber and thereby pump the chemicals out. Fibers which change their shape in response to applied light or magnetic forces or fields may also be used to discharge the chemicals as desired.

Detailed Description Text (42):
Referring now to FIGS. 1a-1f, the new and improved self-repairing fiber reinforced matrix composite and its operation in the field is shown. As depicted in FIG. 1, a hollow fiber containing an adhesive modifying agent and coated with a thin coating material is dispersed within a settable or curable matrix material which may be either a polymer or cementitious material. As shown in FIG. 1b, a loading applied to a shaped article causes strains within the matrix, which in turn cause the fiber to break and the matrix to crack. This causes the modifying chemical agent disposed within the hollow fiber to be released into the vicinity of the crack in the matrix as shown in FIG. 1b. The modifying agent flows and fills the void as shown in FIG. 1e and eventually cures to rebond the fiber to the matrix and to repair the fiber to itself as shown in FIG. 1f. This schematically illustrates the modified fiber concept of the present invention.

Detailed Description Text (43):
Referring now to FIGS. 2a-2e, a similar smart fiber repair embodiment is depicted wherein the smart hollow fibers contain anticorrosive modifying agent and are coated with fibers which are pH sensitive. These smart fibers are disposed within the matrix adjacent the rebar reinforcement by selectively positioning them adjacent the rebar as the matrix is poured into the concrete mold or the rebar can actually be wrapped with the hollow fibers which have been previously banded together as a web or tape. In accordance with this matrix composite construction, the anticorrosion filled smart fibers are disposed immediately adjacent the rebars. The anticorrosive chemical compounds are not released to protect the rebars unless or until the exchange has occurred in the vicinity of the rebar, either due to chloride iron infiltration or carbon dioxide intrusion. The advance of corrosive chemicals breaks down the pH versus sensitive coating on the smart fiber, releasing the protective anticorrosive agent to protect the rebar from corrosion by the environmental chemicals found in FIGS. 2c-2e.

Detailed Description Text (44):
Referring now to FIGS. 3a-3c, the smart fiber matrix is shown in operation in plain and in antifreeze modifying agent disposed within the hollow fibers. A water-based antifreeze expands as it cools to force its way out of the pores in the hollow fiber, thereby dislodging the coating, if present, and permitting the antifreeze to exit into the local environment of the matrix. As shown in FIGS. 3b-3c, the release of the antifreeze into the matrix lowers the freezing temperature of moisture in the materials within the matrix preventing freeze/thaw damage from occurring to the matrix.

Detailed Description Text (45):
Referring now to FIG. 4, a debonding of a coated fiber is shown as a mechanism for releasing the modifying agent contained within the smart fiber into adjacent areas of the matrix. This can occur, for example, where there is coating applied to the smart fiber to retain the modifying agent within the fiber interior as a higher affinity for the surrounding matrix in a cured state than to the fiber. Accordingly, debonding of the fiber from its coating allows the pores to become open to permit chemical release.

Detailed Description Text (46):
Referring now to FIG. 5, there is illustrated in the embodiment wherein modifying agent release is caused by. torting, twisting or other load changes which cause a dimensional change in the shape of the hollow fiber, which in turn forces the modifying agent out into the surrounding matrix. These torting, twisting or other loads placed on the fiber may cause local debonding of the fiber from its coating, permitting release as shown in FIG. 4 or a mechanical forcing of the contents of the fiber through the pores, which in turn causes dislodgment of the coating may also occur.

Detailed Description Text (47):
Referring now to FIGS. 6a and 6b, the application of the compressive load on a twisted fiber bundle can cause debonding of the coating from the twisted fibers forcing fluid contained within the hollow spaces of the fiber through the fiber pores and into the surrounding matrix.

Detailed Description Text (53):
FIG. 12 is an alternate embodiment wherein waves of low frequency such as seismic waves may pass through the matrix in such a manner as to cause debonding of the fiber from a coating or uncoated fibers may cause the modifying agent to exit from pores disposed within the fiber matrix disposed within the hollow fiber.

Detailed Description Text (57):
Referring now to FIG. 21, the new and improved smart fiber matrix composite materials in accordance with this invention may be used in connection with other matrix protecting practices to provide redundant protection against environmental damage. As depicted in FIG. 21, a cementitious matrix including rebars may include surface coatings and sealants to prevent the ingress of harmful environmental liquids. Calcium nitrite anticorrosion chemicals may be freely mixed within the cement and the smart fiber reinforcements may be disposed immediately adjacent the rebar containing additional anticorrosive modifying agents in accordance with this invention for release as needed when the concentration of corrosion chemicals get sufficiently high to stimulate their release.

Detailed Description Text (60):
As shown in FIG. 23b, once the ingress of moisture is sensed at the impermeable barrier layer, an electrical signal may be sent through the inner barrier layer, causing discharge or migration of cat ions from the middle layer towards the rebar, which causes a coating on the smart fiber to be broken down to permit release of the modifying agent contained therein of anticorrosion chemicals into the immediate vicinity of the rebar to prevent corrosion.

Detailed Description Text (62):
In FIG. 23d, an alternate aspect is provided wherein the barrier is electrified to provide a galvanic cell in the immediate region between the barrier layer and the rebar. A counter galvanic cell is created about the hollow middle fibers which contain a modifying chemical inside the buffer zone, which in turn can release moisture binding hydroscopic chemicals in response to application of electrical charges or may release anticorrosive chemicals. In accordance with FIG. 23e, the

hollow fibers disposed within the barrier buffer zone may include zinc ions which will migrate and coat the rebar in a galvanizing or electric lading action by application of the voltage between the barrier and rebar.

Detailed Description Text (66):
Referring now to FIGS. 27a and 27b, another glass fiber embodiment is shown wherein an assembly including an outer hollow glass tube filled with adhesive modifying agent and including an optical fiber therein and a middle fiber therein provide a special matrix composite. As shown in FIG. 27b, in response to an applied load, the middle fiber bending assist in breaking the outer glass tube to thereby release the repairing adhesive to the matrix. The optical fiber polymer may be bent or stretched and light lost to cladding coating on the fiber may be detected outside the matrix to determine bending of the fibers and possible microcracking therein.

Detailed Description Text (70):
Referring now to FIG. 30c, the new and improved smart matrix material is shown in a rebonded condition wherein the interior modifying agent, in this case an adhesive, has leached into the surrounding matrix to repair crack, to bond the matrix to itself, and to bond the coating to the matrix and the coating to the fiber. This restores the overall integrity of the composite, and in some cases, may lead to actual increases in overall strength and performance for the rebond material.

Detailed Description Text (72):
In accordance with the present invention, other embodiments for using the self-repairing fiber reinforcement smart matrix composite matrix materials described herein will be readily apparent to those skilled in this art. For example, employing ceramic matrices such as a hydroxyapatite ceramic minerals and reinforcing hollow fibers containing bio-compatible crack repairing adhesives may be used in joint replacements or as shaped articles for prosthetic devices. In this manner, biomedical embodiments for the smart matrix composite materials possessing the self-repair properties may be used to provide improved or extended fuselage to prosthetic devices and bone replacements. Stress load fractures occurring within the artificial bone or joint segment will self-repair in accordance with the principles of this invention.

Detailed Description Text (75):
In accordance with this invention, the matrix selected may vary, for example, RIBTEC.RTM. mats of stainless steel fibers may be slurry infiltrated with cement, hollow fibers for repair may be included. Under loading, the mat causes the cement to form microcracks, which in accordance with this invention releases the repair adhesives into the matrix to provide a repaired high toughness composite material. Depending on the matrix selected, different fiber properties may be desired, for example, in rigid matrix materials such as cementitious set materials or sintrex ceramic materials more flexible fibers may be desirable, whereas in polymer matrices having inherent elasticity or flexibility, more rigid fibers such as glass or metal fibers may be desired. In addition, it may be desired to use fibers which become brittle over time. Fibers may be connected to each other with flexible parts to ensure that they do not break prematurely during mixing or compounding. Furthermore, chemicals which survive the long periods of time and which survive repeated temperature variations may also be used as the modifying agents. Although several different matrix materials have been disclosed or suggested herein, others may still be used by those skilled in this art. Although a number of different kinds of fibers have also been described, still other fibers might also be used by those skilled in this art in accordance with the principles of this invention. Different modifying agents and different mechanisms for selective release of the modifying agent in response to an external stimuli or internal stresses caused by other external occurrences might also be developed and designed by those skilled in the art given the principles provided herein. Accordingly, all such obvious modifications may be made herein without departing from the scope and spirit of the present invention as defined by the appended claims.

CLAIMS:

9. A shaped article as defined in claim 1, wherein said means for maintaining the modifying agent within the fibers comprises a coating material disposed on said fibers.

15. A shaped article as defined in claim 11, wherein said inorganic matrix material is selected from cement, concrete, ceramic or metal matrix materials.

17. A shaped article as defined in claim 15, wherein said metal matrix material comprises aluminum, iron, lead, copper, steel, bronze phosphor bronze, or brass.

21. A shaped article as defined in claim 9, wherein said coating is selected from chemically sensitive, electrically sensitive or radiation sensitive coatings.

22. A shaped article as defined in claim 21, wherein said chemically sensitive coating is selected from moisture sensitive, pH sensitive, ion sensitive or solvent sensitive coatings.

23. A shaped article as defined in claim 21, wherein said electrically sensitive coating is selected from the group consisting of current sensitive and voltage sensitive coatings.

24. A shaped article as defined in claim 21, wherein said radiation sensitive coating is selected from the group consisting of light sensitive, temperature sensitive and radioactivity sensitive coatings.